Applied Catalysis B: Environmental 202 (2017) 199–206

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Natural microgranular cellulose as alternative catalyst to metal nanoparticles for H_2 production from $NaBH_4$ methanolysis

Nurettin Sahiner[a,b,*], Sahin Demirci[a]

[a] Faculty of Science & Arts, Department of Chemistry, Canakkale Onsekiz Mart University, Terzioglu Campus, 17100, Canakkale, Turkey
[b] Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Terzioglu Campus, 17100, Canakkale, Turkey

ARTICLE INFO

Article history:
Received 17 July 2016
Received in revised form 4 September 2016
Accepted 13 September 2016
Available online 13 September 2016

Keywords:
Natural cellulose catalyst
Modified microgranular/microgel
Renewable H_2 generating cellulose catalyst

ABSTRACT

Herein, we report the utilization of microgranular cellulose as a catalyst in virgin and in modified form to be used as metal free catalyst directly in methanolysis reaction of $NaBH_4$ for hydrogen (H_2) production. Cellulose was modified with epichlorohydrin and then with diethylenetriamine as Cell-EPC-DETA followed by protonation by hydrochloric acid treatment to obtain Cell-EPC-DETA-HCl. The hydrogen generation rates (HGR) of 408 and 2015 mL H_2/g catalyst.min were estimated for bare cellulose, and Cell-EPC-DETA, respectively upon their use as catalysts in the methanolysis reaction of $NaBH_4$. Interestingly, HGR value is almost increased 1.6 fold increased, 3215 mL H_2/(g catalyst min) upon potations. Besides, the activation energies of Cell-EPC-DETA and Cell-EPC-DETA-HCl were determined as 38.2 and 34.4 kJ/mol, respectively that are comparable with the literature. Moreover, the reusability studies of Cell-EPC-DETA and Cell-EPC-DETA-HCl were performed and it was found that there is no decreasing on% conversion for both catalyst, whereas % activity decreased to 61 ± 6, and 65 ± 4% for Cell-EPC-DETA and Cell-EPC-DETA-HCl.

1. Introduction

Cellulose is a renewable, non-meltable, biodegradable natural polymer which is insoluble in most solvents due to hydrogen bonding and high crystallinity. Total production of 1011–1012 tons/year make cellulose the most abundant natural polymer in the world [1,2]. Cellulose is a cheap, biodegradable and renewable polymer which is water insoluble, tough and fibrous nature helps in sustaining the structure of the cell walls of plants, omycetes and algae [3]. Cellulose can also be used as a green source for fabricating biodegradable and biocompatible materials with significance interesting properties by chemical modification or mixing with other components [4]. Effective utilization of cellulose not only decreased the fossil resources crisis but also protects the environment. Due to interesting properties of cellulose, many investigators are focused on their attention on the modification and utilization of cellulose in various applications such as drug delivery systems [5], removal of toxic metals and organic compounds [6], sensor [7], production of alcohol [8].

H_2 is attracting great interest as the most benign energy source owing to its renewable, carbon free, clean and eco-friendly properties [9]. Various types of metal hydrides such as sodium borohydride ($NaBH_4$) [10], ammonia borane (NH_3BH_3) [10], lithium borohydride ($LiBH_4$) [11] or another sources [12,13] have been commonly used as chemical sources for H_2 production. $NaBH_4$ is the most abundantly utilized metal hydride among the all hydrides due to its very well-known non and easy hydrolysis reaction [14], higher hydrogen generation yield rate with 10.9 wt.% Hydrogen content [15], and the availability of feasible methods of regeneration of $NaBH_4$ form its by-products [16]. Many metal catalysts with different formulations based on Ru, Pt, Co and Ni nanoparticles have been employed for the hydrolysis of $NaBH_4$ [10,14,17,18]. Recently, non-metal catalyst for hydrogen generation from $NaBH_4$ have also been started to investigation [19]. Disadvantages of hydrolysis of $NaBH_4$ such as slow and low conversion ability and slow reaction kinetic at lower temperature of hydrolysis of $NaBH_4$ reaction urge researchers to look for new and resourcefulness solvent for hydrogen production [20]. Therefore, in recent years methanolysis of $NaBH_4$ reaction (Eq. (1)) has been also started to use due its better properties than hydrolysis reaction such as higher hydrogen production rates at low temperature, the ability of obtaining methanol

* Corresponding author at: Faculty of Science & Arts, Nanoscience and Technology Research and Application Center (NANORAC), Canakkale Onsekiz Mart University, Terzioglu Campus, 17100, Canakkale, Turkey.
E-mail address: sahiner71@gmail.com (N. Sahiner).

http://dx.doi.org/10.1016/j.apcatb.2016.09.028
0926-3373/

from renewable sources and biomass feedstocks, and The highest amounts of NaBH4 that is soluble in 100 mL methanol is 16.4 g [21]. The methanolysis of $NaBH_4$ is given in Eq. (1).

$$NaBH_4 + 4CH_3OH \rightarrow 4H_2 + NaB(OCH_3)_4 \quad (1)$$

Moreover, the by-product of the methanolysis reaction ($NaB(OCH_3)_4$) does not have the tendency to block the reactor [22,23]. Therefore, the use of $NaBH_4$ as H_2 source and methanol as solvent is reasonable and advantages over the hydrolysis of $NaBH_4$ that require water which is good but also this reaction necessities expensive metal catalysts that are generally toxic and non-renewable, and required some tiresome preparation and elimination problems.

Herein, in this study, we report for the first time the use of the most abundant natural polymer in the world that is cellulose as catalyst after simple chemical modification using epichlorohydrine and diethylenetriamine (Cell-EPC-DETA) to generate energy friendly H_2 production from the methanolysis of $NaBH_4$. The modified microgranular cellulose with amine groups on the structure are protonated with the treatment of hydrochloric acid solution to generated Cell-EPC-DETA-HCl material as catalyst. The prepared Cell-EPC-DETA and Cell-EPC-DETA-HCl were used directly as catalyst in methanolysis reaction of $NaBH_4$ for H_2 production. The various parameters such as the effect of modification, protonation, the amount of catalyst, temperature, and re-usability on H_2 production rate were investigated. Hydrogen generation rate (HGR) values were determined along with the activation parameters such as activation energy (Ea), enthalpy (ΔH), and entropy (ΔS).

2. Experimental

2.1. Materials

Microgranular cellulose (Cell, 2–20 μm, Sigma Aldrich) was used as a main material. Epichlorohydrin (EPC, 99%, Sigma Aldrich), diethylenetriamine (DETA, 99%, Sigma Aldrich) were used as modifying agents, and dimethylformamide (DMF, 99%, Merck) was used as reaction medium. Hydrochloric acid (HCl, 36–38%, Sigma Aldrich) was used for protonation of modified Cell. Distilled water (DI) and acetone (96% technical grade) were used for washing steps. Sodium borohydride ($NaBH_4$, 98%, Merck) was used as a source of H_2, and methanol (99.9%, Sigma Aldrich) was used as reaction medium.

2.2. Modification and protonation of microgranular cellulose

Certain amount of Cell (3 g) was treated with 100 mL 1 M NaOH solution about 2 h for activation of hydroxyl groups (deprotonation) on Cell, followed by extensive washing with DI. Then, the activated Cell (1 g) was dispersed in 40 mL DMF into a 100 mL round bottom flask equipped with a magnetic stirring bar and condenser, followed by addition of 3 mL of EPC in reaction medium. Reaction was continued for 1 h at 90 °C at 750 rpm mixing rate. After that, the 3 mL of DETA was added into reaction medium and reaction was continued for another 1 h at the same mixing rate and temperature and the reaction was stopped. Modified Cell-EPC-DETA was washed with water several times and three times with ethanol by centrifugation ten min at 10 000 rpm. After washing steps, Cell-EPC-DETA were dried using heat gun and then placed into oven at 50 °C for 12 h, and the rried Cell-EPC-DETAs were stored in closed tubes. To protonate the newly formed amine groups on Cell, 0.75 g dried Cell-EPC-DETAs was placed into 50 mL 1 M HCl solution and stirred for 4 h at 750 rpm mixing rate, and washed with DI twice and with acetone twice to obtained Cell-EPC-DETA-HCl. Then, the protonated Cell was using heat gun, and then placed into oven at 50 °C for further drying for 12 h. The both dried Cell-EPC-DETA and Cell-EPC-DETA-HCls were stored in closed tubes for characterization and catalysis reactions.

2.3. The usage of microgranular cellulose as a catalyst

The modified Cells as Cell-EPC-DETA and Cell-EPC-DETA-HCls were used as catalyst for the methanolysis reaction of $NaBH_4$ for H_2 production. Briefly, certain amount catalyst (50 mg) was dispersed in 20 mL methanol with magnetic stirrer in 50 mL round bottom flask at 25 °C. Then, 125 mM $NaBH_4$ (0.0965 g) was placed into the reaction medium and the evolved H_2 production under 1000 rpm mixing rate was recorded with time.

Various parameters such as the effect of catalyst amounts e.g., 0, 10, 25, 50, and 100 mg Cell-EPC-DETA-HCls, $NaBH_4$ amounts, 31.3, 62.5, 125, 250, and 500 mM $NaBH_4$, and the reaction temperatures; −10, 0, 10, 25, and 40 °C were investigated. Activation parameters such as E_a, ΔH, ΔS, and also HGR and TOF values were also calculated and compared each other for methanolysis reaction of $NaBH_4$ catalyzed by Cell-EPC-DETA and Cell-EPC-DETA-HCls and with the literature.

2.4. Re-usability and regeneration studies of microgranular cellulose as a catalyst in $NaBH_4$ methanolysis reaction

The re-usability studies of Cell-EPC-DETA and Cell-EPC-DETA-HCl done by repetitive using of the same catalyst in freshly prepared NaBH4 methanol solutions. Briefly, certain amount of catalyst (50 mg) was placed into 50 mL round bottom flask with 20 mL methanol and 0.0965 g $NaBH_4$ and H_2 production volumes with time was measured. The same amount of $NaBH_4$ was added into reaction medium directly after finishing H_2 production for the first time and this new NaBH4 introduction to the rector was repeated for five times. Then, the change in% activation and % conversion were measured and compared for both catalysts, Cell-EPC-DETA and Cell-EPC-DETA-HCl. Moreover, Cell-EPC-DETA-HCl catalyst was regenerated after every fifth usage with using 20 mL of 1 M HCl solution. Then, the reusability studies of regenerated Cell-EPC-DETA-HCl catalyst were tested five times each.

3. Results and discussion

3.1. Preparation and characterization of cell-EPC-DETA and cell-EPC-DETA-HCl

As epoxy groups are very reactive under alkaline conditions, by the activation of microgranular Cell carried out with alkaline solution generated hydroxyl groups can readily react with EPC and corresponding schematic presentation of activation of Cell is illustrated in Fig. 1(a). And the obtained Cell-EPC possessing another active chloride groups on allowed one more modification readily. For the functionalization of Cell, these chloride groups containing Cell-EPC reacted with DETA at the same reaction conditions and schematic presentation is given in Fig. 1(b). As can be seen on Fig. 1(b), amine functionalized Cell provide some protonated some more amine groups that are protonable. Due to nature of reaction, the generated HCl can protonate some of amine groups but not all of them. Therefore, further protonation reaction was performed on Cell-EPC-DETA by HCl treatments, and schematic presentation of reaction is given in Fig. 1(c). It was predicted that all amine groups on Cell-EPC-DETA can be readily protonated with the HCl treatment reactions. Optic microscope images of bare microgranular Cell and protonated Cell-EPC-DETA-HCl were taken and illustrated in Fig. 2(a) and (b) respectively. It was clearly seen from optic microscope images that, there are changes on surface of cellulose after

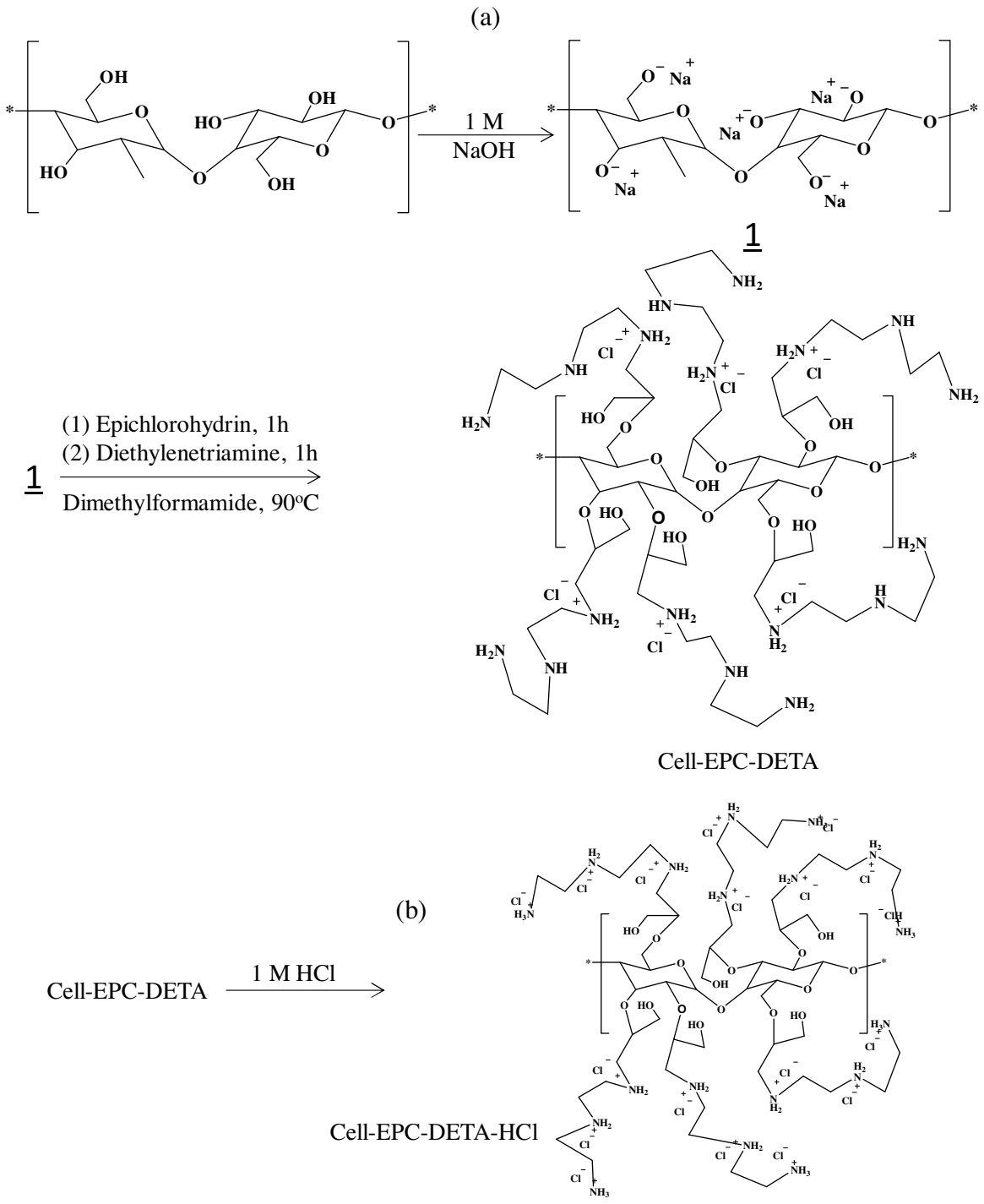

Fig 1. The mechanism of modification of microgranular cellulose with diethylinetriamine (DETA).

modification microgranular Cell to Cell-EPC-DETA-HCl. As the surface of cellulose was amine modified upon modification reaction by DETA that contains two primary and one secondary amine groups, and these amine groups provide strong polyelectrolyte characteristics by protonation or quarternization reaction by HCl treatments [24], and positively charges at equilibrium conditions will be generated [25]. Therefore, these positively charged catalyst show faster catalytic performances due to the faster interaction ability with negatively charged reactant species [19]. Therefore, to confirm the change on surface charge of bare cellulose after modification with DETA and corresponding zeta potential graph is given in Fig. 2(c). The surface charge of DETA modified microgranular Cell, Cell-EPC-DETA was measured $+15.2 \pm 1.4$ mV whereas surface charge of virgin microgranular Cell was measured as -13.1 ± 1.7 mV. Upon further treatment of Cell-EPC-DETA with HCl for the protonation of the newly amine groups on Cell-EPC-DETA-HCl, the zeta potential value $+33.6 \pm 2.1$ mV was measured confirming the modification reactions.

To further corroborate the modification reaction, FT-IR spectra of microgranulars Cell, Cell-EPC-DETA and Cell-EPC-DETA-HCl were taken and the corresponding spectra were given in Fig. 2(d). In these three spectra, the stretching frequencies at 3412, 2918, 1161, and 1048 cm^{-1} that were observed are the characteristic peaks of cellulose [26]. The peaks in the three spectra are rather similar

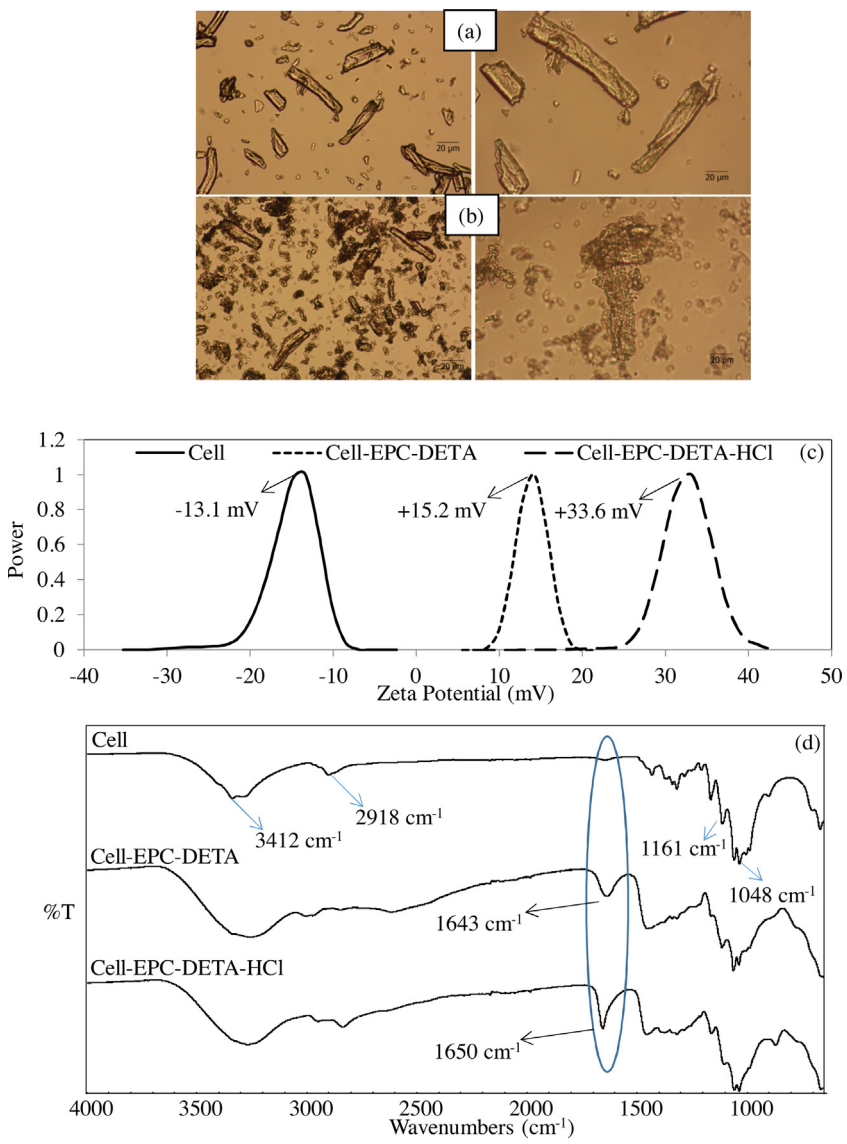

Fig. 2. The protonation of modified microgranular Cell, Cell-EPC-DETA, and (b) the zeta potential measurements of virgin, modified and protonated microgranular, and (c) FT-IR spectra of microgranulars Cell, Cell-EPC-DETA, and Cell-EPC-DETA-HCl.

and one newly formed peak at 1643 cm^{-1} was observed on spectra of Cell-EPC-DETA that coming from amine groups of modifying agents, and this peak increased intensity and shifted to 1650 cm^{-1} wave number upon the treatment of Cell-EPC-DETA with HCl further confirm the protonation reactions.

3.2. The methanolysis of $NaBH_4$ catalyzed be microgranular based cellulose

3.2.1. Effect of catalyst

Among the all chemical hydrides that are used for H_2 production, $NaBH_4$ is assumed to be the hydride most convenient one as a H_2 source due to its great advantages such as non-flammability and stability in air, commercial availability, side product recyclability, and high H_2 storage efficiencies [9]. The hydrolysis reaction of $NaBH_4$ generally for high H_2 generation rates required expensive and toxic metal catalysts. And the hydrolysis reaction is very catalyzed by metal nanoparticle are very slow at low temperatures and sometimes it is impossible below 0 °C due to the ice formation. Therefore, in the cold climates where the most of time of the year where the temperature is well below 0 °C make impossible to work for H_2 powered devices where the source is $NaBH_4$ and H_2 production is obtained from the catalytic reaction. Therefore, the temperature of H_2 production reaction conditions also have significant role for real time applications [20]. Thus, many researchers have focused on the different solvents for obtained effective H_2 production at low temperature, and used alcohols such as methanol instead of water due to its lower freezing point, −97.6 °C [23]. The self-methanolysis and catalyzed by virgin Cell of $NaBH_4$ reaction was carried out at 25 °C and results are given in Fig. 3(a). As can be seen from Fig. 3(a), self methanolysis of $NaBH_4$ produced about 250 mL H_2 in 30 min, whereas the methanolysis of $NaBH_4$ catalyzed by 50 mg virgin microgranular Cell produced the same amount of about 250 mL H_2 in 24 min, and the HGR values of virgin microgranular Cell was calculated as 408 mL H_2/(g of catalyst min). The virgin microgranular Cell therefore cannot be considerable as effective catalyst for the methanolysis of $NaBH_4$ for H_2 production. On the other hand, interestingly, the modification of Cell with DETA and the protonation of this DETA modified microgranular Cell increased the catalytic performance of the materials on methanolysis reaction of $NaBH_4$ tremendously, and corresponding graph is given in Fig. 3(b). It can be clearly seen form Fig. 3(b) that the

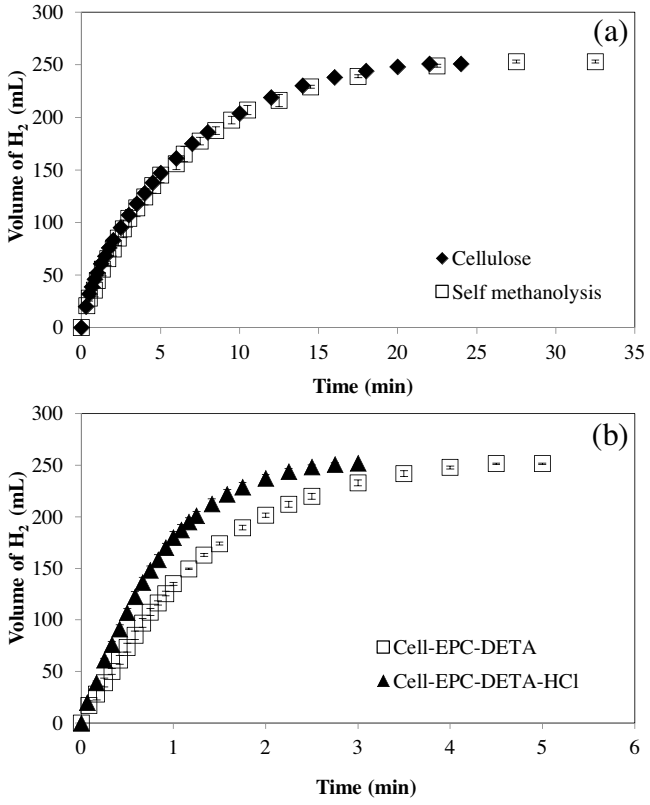

Fig. 3. (a) The H_2 production via self methanolysis of $NaBH_4$, and in the presence of microgranular Cell as catalyst, and (b) the effects modification on the catalytic performances of microgranular based Cell catalysts (Cell-EPC-DETA and Cell-EPC-DETA-HCl)on H_2 production from the methanolysis of $NaBH_4$ [Reaction condition, 50 mg catalyst, 20 mL methanol, 0.0965 g $NaBH_4$, 25 °C, 1000 rpm].

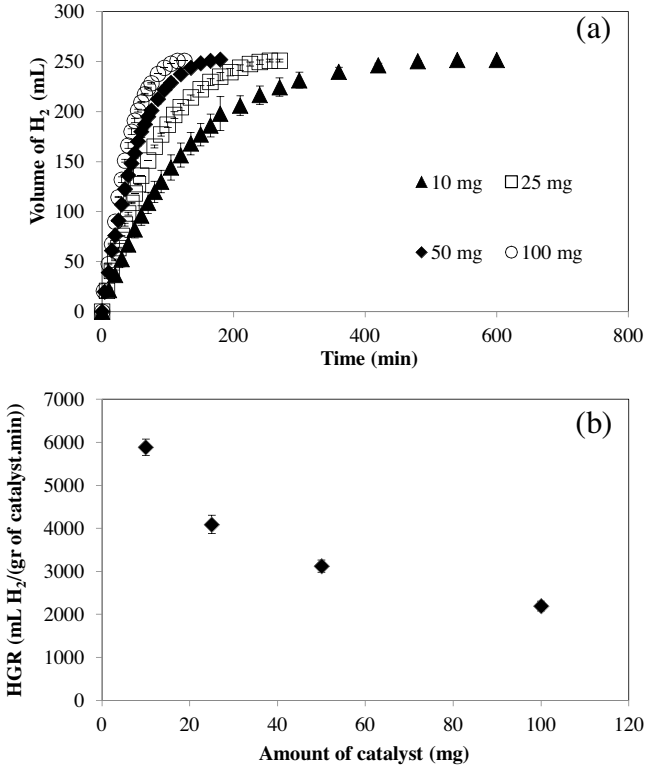

Fig. 4. (a) The effect of the amount of catalyst on $NaBH_4$ methanolysis, and (b) the comparison of HGR values for the methanolysis reaction catalyzed by different amounts of Cell-EPC-DETA-HCl catalyst [Reaction condition, 50 mg catalyst, 20 mL methanol, 0.0965 g $NaBH_4$, 25 °C, 1000 rpm].

catalyst performance of microgranulars of Cell-EPC-DETA and Cell-EPC-DETA-HCl much better than self-methanolysis and unmodified Cell catalyzed methanolysis of $NaBH_4$ reaction with production of about 250 mL H_2 in 5 and 3 min respectively. Moreover, upon comparison of HGRs, the Cell-EPC-DETA-HCl provide faster H_2 production rate in comparison to Cell-EPC-DETA with HGR values of 3215 and 2015 mL H_2/(g of catalyst min), respectively. It is important to note that the HGR values of Cell-EPC-DETA-HCl are 1.6 fold better than Cell-EPC-DETA and approximately 8 fold better than bare Cell catalyzed methanolysis of $NaBH_4$ upon using the same amounts of catalyst (50 mg). The positive charge on Cell-EPC-DETA created by protonation of amine groups provides better catalytic performances for methanolysis of $NaBH_4$. It was also observed for hydrolysis reaction of $NaBH_4$ in literature that positively charged amine species as metal-free catalysts showed good catalytic activity for the hydrolysis reaction of $NaBH_4$ [19]. It was suggested that the BH_4^- anions can react readily with the positively charged amine groups for the production of H_2 [19]. Moreover, similar results were also observed in methanolysis reaction of $NaBH_4$ that is better catalyzed by positively charged amine groups containing metal-free microgel catalyst [27].

3.2.2. *Effect of amount of catalyst on H_2 production*

As Cell-EPC-DETA-HCl catalyst perform better than unmodified Cell and Cell-EPC-DETA, the amount of this catalyst on methanolysis reaction of $NaBH_4$ was investigated by varying the amounts of catalysts and results are illustrated in Fig. 4(a). As can be seen form the figure, 10, 25, 50, and 100 mg of Cell-EPC-DETA-HCl were used for the same amounts of $NaBH_4$ methanol solutions, and the generated H_2 with time graphs are constructed for each amounts of catalyst. It is obvious that the increase in used amounts of catalyst amount provide faster H_2 production rates with each catalyst producing the same amount of H_2 (about 250 mL) at the same reaction conditions. This amount of H_2 productions were completed in 600, 270, 180, and 125 s by the use of 10, 25, 50, and 100 mg Cell-EPC-DETA-HCl catalyst, respectively. The calculated HGR values with the varying amounts of catalyst were given in Fig. 4(b), and as it can apparently be seen, HGR values decreased with the increasing amount of the used catalyst, and HGR values were calculated as 5886 ± 193, 4090 ± 214, 3125 ± 142, and 2193 ± 112 mLH_2/(g of catalyst min) for 10, 25, 50, and 100 mg catalyst of Cell-EPC-DETA-HCl, respectively. The reduction in HGR with the increase in the amount of Cell-EPC-DETA-HCl catalyst can be attributed to the existence of excess amounts of catalyst in comparison to the low amount of reactant (96.5 mg $NaBH_4$). As the quaternary amine functional groups are playing the essential role in the methanolysis reaction, the increase their numbers with the increasing amounts of catalyst increases the competition for the same amount of reagents ($NaBH_4$) resulting in a reduction in HGR [28,29].

3.2.3. *Effect of temperature on H_2 production*

The effect of temperature on H_2 production from the methanolysis of $NaBH_4$ catalyzed by Cell-EPC-DETA and Cell-EPC-DETA-HCl microgels was investigated to determine and comparison of the activation parameters such as activation energy (E_a), enthalpy (ΔH) and entropy (ΔS) by conducting the methanolysis reaction at five different temperatures; −10, 0, 10, 25, and 40 °C. The produced H_2 volume versus reaction time for $NaBH_4$ methanolysis at different temperature in the presence of 50 mg Cell-EPC-DETA and by 50 mg Cell-EPC-DETA-HCl are given in Fig. 5(a) and (b) respectively. In the methanolysis of $NaBH_4$ catalyzed by 50 mg Cell-EPC-DETA at -10 ± 0.1 °C with 241 mL H_2 production was accomplished in 65 min. On the other hand, for the methanolysis reaction carried

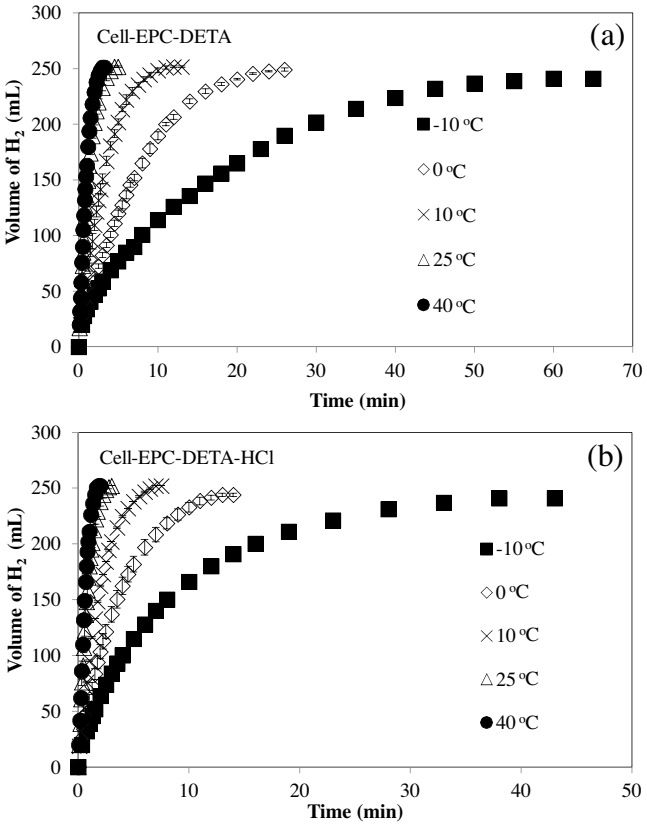

Fig. 5. The effect of temperature on the methanolysis of $NaBH_4$ catalyzed by (a) Cell-EPC-DETA and (b) Cell-EPC-DETA-HCl [Reaction condition, 50 mg catalyst, 20 mL methanol, 0.0965 g $NaBH_4$, 1000 rpm].

out at the other temperatures are significantly fast as the H_2 production of approximately 250 ± 2 mL was accomplished in 26, 13, 5, and 2.75 min for 0 ± 0.1, 10 ± 0.1, 25 ± 1, and 40 ± 1 °C respectively. For $NaBH_4$ methanolysis catalyzed by 50 mg Cell-EPC-DETA-HCl at different temperatures; −10, 0, 10, 25, and 40 °C can be considered better than the methanolysis reactions of Cell-EPC-DETA catalysts at every temperature with the generation of approximately 250 ± 2 mL H_2 production at 43, 14, 7.5, 3, 2 min respectively. It obvious that, although the same amount of unprotonated and protonated modified microgranular Cell based catalysts were used (50 mg), and the same amount of $NaBH_4$ (0.0965 g) in the same volume of methanol (20 mL) were used at every reaction temperature, the H_2 production rate increased linearly with the increase in reaction temperature from −10 to 40 °C with protonated (Cell-EPC-DETA-HCl) being more effective.

Then, the activation parameters such as for Cell-EPC-DETA and Cell-EPC-DETA-HCl catalyzed $NaBH_4$ methanolysis were determined from the Arrhenius (Eq. (3)) and Eyring (Eq. (4)) equations.

$$\ln(k) = \ln(A) - E_a/RT \quad (3)$$

$$\ln(k/t) = -(\Delta H/R)(1/T) + \ln(k_B/h) + \Delta S/R \quad (4)$$

where, k is the reaction rate constant and was calculated according to a zero-order kinetic expression, E_a is the activation energy, T is the absolute temperature, k_B is the Boltzmann constant (1.381×10^{-23} J K^{-1}), h is Planck's constant (6.626×10^{-34} J s), ΔH is the activation enthalpy, ΔS is the entropy and R is the gas constant (8.314 J K^{-1} mol^{-1}). The Arrhenius (ln(k) vs 1/T plot) and Eyring (ln(k/t) vs 1/T plot) plots for $NaBH_4$ methanolysis catalyzed by Cell-EPC-DETA and Cell-EPC-DETA-HCl are given in Fig. 6. The calculated E_a from Arrhenius and ΔH, ΔS from Eyring plots for both Cell-EPC-DETA and Cell-EPC-DETA-HCl catalysts for methanolysis of $NaBH_4$ reaction are given in Table 1. Moreover, the activation parameters for the microgranular cell based catalyst were compared with some of the activation parameters reported in the literature. The calculated E_a value of Cell-EPC-DETA-HCl catalyst was found as 30.8 kJ/mol that is lower than E_a value of Cell-EPC-DETA catalyst (38.7 kJ/mol). Besides, enthalpy and entropy values of Cell-EPC-DETA-HCl catalyst were calculated as 27.8 kJ/mol, −178.9 J/mol K were also observed better than Cell-EPC-DETA catalyst that 35.5 kJ/mol, −158.1 J/mol K, respectively The Ea value of the methanolysis reaction of $NaBH_4$ catalyzed by Cell-EPC-DETA and Cell-EPC-DETA-HCl catalysts with 30.8 and 38.7 kJ/mol are lower than some hydrolysis reactions of $NaBH_4$ catalyzed by metal nanoparticle containing PEI-M (M:Ni) composites [10], and even comparable for other hydrolysis of $NaBH_4$ reactions [20,29,30]. The methanolysis of $NaBH_4$ reaction catalyzed by Cell-EPC-DETA and Cell-EPC-DETA-HCl catalysts with 30.8 and 38.7 kJ/mol are found to be lower than some of the metal catalyzed alcoholysis reactions reported in the literature [20]. Moreover, the methanolysis of $NaBH_4$ reaction catalyzed by Cell-EPC-DETA and Cell-EPC-DETA-HCl catalysts with 30.8 and 38.7 kJ/mol activation energies are also better than some of the other catalyst systems such as hydrolysis reaction of $NaBH_4$ and MgH_2 [31–34]. This results shows that these natural microgranular Cell based polymeric catalyst as an environmentally begin, resourceful and catalytically comparable to more expensive and toxic metal nanoparticle based catalyst or other catalyst systems [35].

3.3. Re-usability and regeneration studies of microgranular cell based catalyst in $NaBH_4$ methanolysis

The re-usability of any catalyst determines the its' faith for industrial applications. Therefore, re-usability of Cell-EPC-DETA and CEll-EPC-DETA-HCl catalyst systems for the methanolysis reaction of $NaBH_4$ were tested five times in a row, and their % conversion and % activities were compared. The % conversion was calculated from conversion of $NaBH_4$ to H_2, and % activity was calculated by taking the ratio of initial H_2 production rates to the following H_2 production rates after each use, and the corresponding graphs for each catalysts were demonstrated Fig. 7(a) and (b). The re-usability studies of Cell-EPC-DETA is given in Fig. 7(a), and it was shown that there is no decrease for % conversion of $NaBH_4$ to H_2 in the methanolysis reaction with using same catalyst of Cell-EPC-DETA for five times, repitetively, whereas the % activity decreased from 100 to 94 ± 1, 82 ± 2, 74 ± 4, 61 ± 4% values after second, third, fourth and fifth usages. The re-usability of Cell-EPC-DETA-HCl was also demonstrated in Fig. 7(b), and almost similar results to the re-usability results of Cell-EPC-DETA catalyst was obtained. For Cell-EPC-DETA-HCl as a catalyst in methanolysis reaction of $NaBH_4$ also there is no decrease on% conversion of $NaBH_4$ to H_2. On the other hand, the % activity of Cell-EPC-DETA-HCl on methanolysis of $NaBH_4$ reaction decreased from 100 to 96 ± 3, 87 ± 4, 78 ± 6, 65 ± 4% by repetitive use of the catalyst second, third, fourth, and fifth times, respectively. So, the protonation of catalyst provides a little better catalytic performance than the unprotonated catalyst at fifth usages: 65 ± 4% for Cell-EPC-DETA-HCl versus 61 ± 6% for Cell-EPC-DETA. Moreover, the Cell-EPC-DETA-HCl catalyst was regenerated after treating with 20 mL of 1 M HCl solution as a Cl^- source for anion exchange with produced borate anion from $NaBH_4$ methanolysis and used reusability studies five times each. The corresponding graph of regeneration studies of Cell-EPC-DETA-HCl catalyst is given in Fig. 7(c). As can be seen in Fig. 7(c), 1st regeneration of Cell-EPC-DETA-HCl catalyst provide increasing of % actvity of catalyst from 70 ± 2 to 98 ± 3% and after 5th usage of catalyst % activity decreased to 63 ± 4%. The 2nd regeneration of

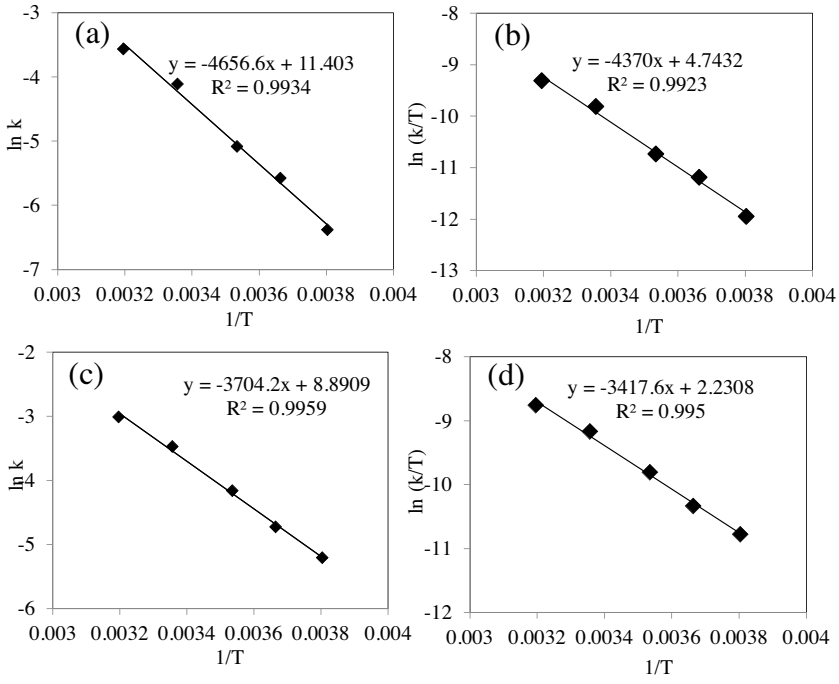

Fig. 6. (a) Arrhenius, (b) Eyring graphs of Cell-EPC-DETA and (c) Arrhenius, (d) Eyring graphs of Cell-EPC-DETA-HCl.

Table 1
The activation parameters, E_a, ΔH, and ΔS, for the methanolysis of $NaBH_4$ catalyzed by Cell-EPC-DETA, and Cell-EPC-DETA-HCl.

Material	$NaBH_4$	Ea (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)	REF
Cell-EPC-DETA	Methanolysis	38.7	35.5	−158.1	This study
Cell-EPC-DETA-HCl	Methanolysis	30.8	27.8	−178.9	This study
PEI-Ni composite	Hydrolysis	38.3	34.8	−186	[10]
Ru/Al_2O_3 pellets	Hydrolysis	41.8	–	–	[18]
	Methanolysis	51			
Au/Ni bimetallic nanoparticles	Hydrolysis	30	–	–	[25]
TiO_2	Hydrolysis	44	–	–	[26]

catalyst increased % activity from 63 ± 4 to 95 ± 4% and after 5th usage of catalyst % activity decreased to 61 ± 1%. The 3rd, 4th and 5th regeneration of catalyst increased % activity from 61 ± 1, and 57 ± 3% to 90 ± 6 and 82 ± 4% respectively. As suggested in literature, the BH_4^- anions react easily with positively charged amine groups for the production of H_2 [19]. The% activity of used catalyst Cell-EPC-DETA-HCl decreased after each usage of reusability studies. This decrease can be explained with the Cl^- anions exchanging with tetramethoxyboron anions and interacting with the positively charged amine groups on the catalyst as the progress of the reaction the concentration of tetramethoxyboron in medium is increased [27,36]. On the other hand, as explained the treatment of five times used Cell-EPC-DETA-HCl with HCl solution provide tetramethoxybborate anions exchanging again with Cl^- anions and make it possible to increase catalytic activity again. It was also shown here that, the%activity of Cell-EPC-DETA-HCl catalyst was increased by regeneration with HCl.

4. Conclusion

Here, for the first time a natural polymer, microgranular Cell were modified chemical DETA and HCl treatment for protonation of the newly formed amino groups was used as catalyst in methanolysis of $NaBH_4$ for H_2 production that is another sentimentally benign fuel source. The chemical modification of Cell was confirmed by zeta potential measurements, titration curves and from FT-IR spectra. The microgranular Cell upon directly used as catalyst in the methanolysis of $NaBH_4$ can produce about 251 mL H_2 in 24 min that is about the same without any catalyst. Surprisingly, the modification of Cell with DETA provide much better catalytic performance than virgin Cell by generating 251 mL H_2 in 5 min, and furthermore upon protonation of DETA modified Cell (Cell-EPC-DETA-HCl), a superior catalytic performances were obtained by producing the same amount of H_2 in 3 min. The calculated HGR values show that Cell-EPC-DETA-HCl (3125 mL H_2/(g of catalyst min)) approximately 1.6 fold better that Cell-EPC-DETA (2015 mL H_2/(g of catalyst min)) and 8 fold better than bare cell (408 mL H_2/(g of catalyst min)). Moreover, the calculated activation energies value of 30.8, and 38.7 kJ/mol for Cell-EPC-DETA-HCl, and Cell-EPC-DETA, respectively are even comparable with the metal nanoparticle catalyzed hydrolysis and methanolysis reactions for H_2 production from $NaBH_4$. Moreover, the re-usability studies suggest that after five reuse of the same catalyst in methanolysis of $NaBH_4$, the % conversion was not effected for both catalysts of Cell-EPC-DETA and Cell-EPC-DETA-HCl, whereas % activity decreased from 100% to 61 ± 6% for Cell-EPC-DETA, and 100%–65 ± 4% for Cell-EPC-DETA-HCl after fifth usage. Interestingly, the % activity values of Cell-EPC-DETA-HCl catalyst can increase with regeneration reaction with HCl after fifth usage. The Cell-EPC-DETA-HCl catalyst can show more than 90% activity till four times regeneration. Therefore, microgranular Cell as a renewable, natural and most abundant biopolymer in the world, can be simply modified and used as an efficient catalyst in the production of another greener energy source, H_2 production from methanolysis of $NaBH_4$. In addi-

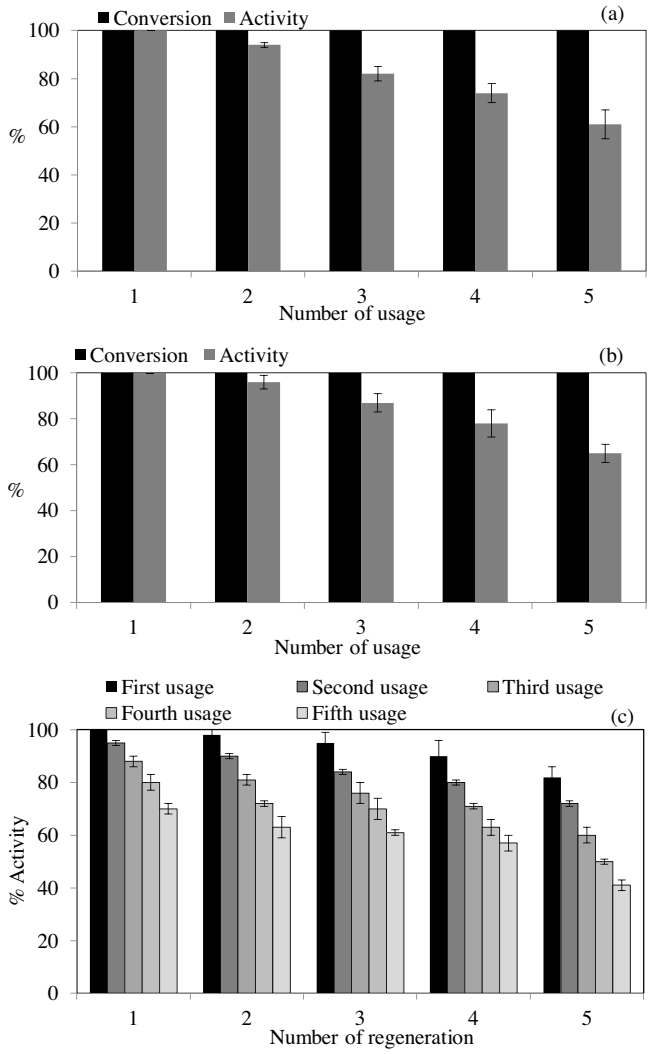

Fig. 7. The reusability of (a) Cell-EPC-DETA, (b) Cell-EPC-DETA-HCl and (c) regeneration of Cell-EPC-DETA-HCl catalysts for methanolysis of $NaBH_4$. [Reaction condition, 50 mg catalyst, 20 mL methanol, 1000 rpm].

tion to the ability to tune the functionalities on the microgranular Cell based catalyst for designing of the next generation of H_2 production systems, the ability of these H_2 generation systems that can operate even at lower temperatures e.g., below 0 °C using of $NaBH_4$ in methanol is a significant contribution to the H_2 powered applications in cold climates, boosting the use of these kinds of systems for the next generation future application potentials.

Acknowledgements

This work is supported by the Scientific and Technological Research Council of Turkey (115M021).

References

[1] T. Huber, J. Mussig, O. Curnow, S.S. Pang, S. Bickerton, M.P. Staiger, J. Mater. Sci. 47 (2012) 1171–1186.
[2] K.E. Perepelkin, Fibre Chem. 36 (2004) 161–176.
[3] P.J.M. Suhas GuptaV.K. Carrott, R. Singh, M. Chaudhary, S. Kushwaha, Bioresour. Technol. 216 (2016) 106–1076.
[4] A. Potthast, T. Rosenau, P. Kosma, Polysaccharides II 205 (2006) 1–45.
[5] F. Zhang, W. Wu, X. Zhang, X. Meng, G. Tong, Y. Deng, Cellulose 23 (2016) 415–425.
[6] H. Ge, H. Huang, M. Xu, Q. Chen, Cellulose (2016), http://dx.doi.org/10.1007/s10570-016-0973-3.
[7] S.W. Lee, J.H. Kim, J. Kim, H.S. Kim, Chin. Sci. Bull. 54 (2009) 2703–2707.
[8] V. Deshpande, S. Keskar, C. Mishra, M. Rao, Enzyme Microb. Technol. 8 (1986) 149–152.
[9] S.S. Muir, X.D. Yao, Int. J. Hydrogen Energy 36 (2011) 5983–5997.
[10] S. Demirci, N. Sahiner, Fuel Process. Technol. 127 (2014) 88–96.
[11] W. Cai, H. Wang, L. Jiao, Y. Wang, M. Zhu, Int. J. Hydrogen Energy 38 (2013) 3304–3312.
[12] J.M. Huang, L.Z. Ouyang, H. WenY.J. Wang, J.W. Liu, Z.L. Chen, M. Zhu, Int. J. Hydrogen Energy 39 (2014) 6813–6818.
[13] L.Z. Ouyang, J.M. Huang, C.J. Fang, Q.A. Zhang, D.L. Sun, M. Zhu, Int. J. Hydrogen Energy 37 (2012) 12358–12364.
[14] N. Sahiner, A.O. Yasar, N. Aktas, J. Ind. Eng. Chem. 23 (2015) 100–108.
[15] H. Zhong, H. Wang, J.W. Liu, D.L. Sun, F. Fang, Q.A. Zhang, L.Z. Ouyang, M. Zhu, J. Alloys Compd. 680 (2016) 419–426.
[16] L.Z. Ouyang, H. Zhong, Z.M. Li, Z.J. Cao, H. Wang, J.W. Liu, X.K. Zhu, M. Zhu, J. Power Source 269 (2014) 768–772.
[17] Y. Kojima, Y. Kawai, H. Nakanishi, S. Matsumoto, J. Power Source 135 (2004) 36–41.
[18] Y.H. Huang, C.C. Su, S.L. Wang, M.C. Lu, Energy 46 (2012) 242–247.
[19] L. Lu, H. Zhang, S. Zhang, F. Li, Angew. Chem. Int. Edit. 54 (2015) 9328–9332.
[20] C.C. Su, M.C. Lu, S.J. Wang, Y.H. Huang, RSC Adv. 2 (2012) 2073–2079.
[21] D.M.F. Santos, C.A.C. Sequiera, Fuel 15 (2011) 3980–4001.
[22] R.E. Davis, J.A. Gottbrath, J. Am. Chem. Soc. 84 (1962) 895–898.
[23] C.T.F. Lo, K. Karan, B.R. Davis, Ind. Eng. Chem. Res. 46 (2007) 5478–5484.
[24] V. Bütün, Polymer 44 (2003) 7321–7334.
[25] C. Sardo, R. Farra, M. Licciardi, B. Dapas, C. Scialabba, G. Giammona, M. Grassi, G. Grassi, G. Cavallaro, Eur. J. Pharma. Sci. 75 (2015) 60–71.
[26] C.F. Liu, R.C. Sun, A.P. Zhang, J.L. Ren, Z.C. Geng, Polym. Degred. Stabil. 91 (2006) 3040–3047.
[27] N. Sahiner, A.O. Yasar, Fuel Process. Technol. 152 (2016) 316–324.
[28] S. Sahiner, O. Ozay, E. Inger, N. Aktas, Appl. Catal. B. Environ. 102 (2011) 201–206.
[29] N. Sahiner, S. Yildiz, H. Al-Lohedan, Appl. Catal. B. Environ. 166-167 (2015) 145–154.
[30] X. Wang, S. Sun, Z. Huang, H. Zhang, S. Zhang, Int. J. Hydrogen Energy 39 (2014) 905–916.
[31] X. Shen, Q. Wang, Q. Wu, S. Guo, Z. Zhang, Z. Sun, B. Liu, Z. Wang, B. Zhao, W. Ding, Energy 90 (2015) 464–474.
[32] M. Jangir, A. Jain, S. Yamaguchi, T. Ichikawa, C. Lal, I.P. Jain, Int. J. Hydrogen Energy 41 (2016) 14178–14183.
[33] M. Huang, L. Ouyang, H. Wang, J. Liu, M. Zhu, Int. J. Hydrogen Energy 40 (2015) 6145–6150.
[34] J.M. Huang, R.M. Duan, L.Z. Ouyang, Y.J. Wen, H. Wang, M. Zhu, Int. J. Hydrogen Energy 39 (2014) 13564–113568.
[35] D. Xu, Y. Zhang, L. Cheng, L. Zhao, Fuel 134 (2014) 257–262.
[36] L.Z. Ouyang, Y.J. Wen, Y.J. Xu, X.S. Yang, L.X. Sun, M. Zhu, Int. J. Hydrogen Energy 35 (2010) 8161–8165.